

# Electrocaloric effect in BaTiO<sub>3</sub>: a first-principles-based study on the effect of misfit strain

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We address the question of how the electrocaloric effect in epitaxial thin films of the prototypical ferroelectric BaTiO<sub>3</sub> is affected by the clamping to the substrate and by substrate-induced misfit strain. We use molecular dynamics simulations and a first-principles-based effective Hamiltonian to calculate the adiabatic temperature change  $\Delta T$  under different epitaxial constraints. Our results demonstrate that, consistent with phenomenological theory, clamping by the substrate reduces the maximum  $\Delta T$  compared to bulk BaTiO<sub>3</sub>. On the other hand, compressive misfit-strain leads to a strong increase of  $\Delta T$  and shifts the maximum of the electrocaloric effect to higher temperatures. A rather small compressive strain of  $-0.75\%$  is sufficient to obtain a  $\Delta T$  that is larger than the corresponding bulk value.

The electrocaloric (EC) effect manifests itself as temperature change of a dielectric material induced by an applied electric field.<sup>1,2</sup> The electric field increases the order of the electric dipoles, which decreases the entropy of the system and under adiabatic conditions leads to an increase in temperature. When the field is removed the dipoles disorder, which, depending on the process conditions, leads to an increase in entropy and/or a reduction in temperature.

Even though the EC effect has been known for a long time (see e.g. Ref. 1), the observed temperature changes were considered too small to be suitable for applications. However, the recent report of a “giant electrocaloric effect” in Pb(Zr,Ti)O<sub>3</sub> thin films by Mischenko *et al.*<sup>3</sup> has stimulated extensive work in this area, and has established the EC effect as an attractive alternative for the design of future cooling devices.<sup>4</sup>

The large EC temperature change that is observed in thin films is mostly due to the larger electric fields that can be applied compared to bulk ceramics.<sup>2</sup> However, it is also well known that the ferroelectric properties of thin film materials are strongly affected by substrate-induced clamping and misfit strain.<sup>5,6</sup> For example, thin films of BaTiO<sub>3</sub> (BTO), a typical textbook model ferroelectric, exhibit strongly enhanced ferroelectric properties.<sup>7</sup> Furthermore, epitaxial strain not only affects the electric polarization and ferroelectric transition temperatures, but also results in a different sequence of phase transitions compared to those observed in the unstrained bulk case.<sup>8,9</sup> Using phenomenological Landau-Devonshire theory, it has been shown that epitaxial strain also affects the EC temperature change in BTO and related materials.<sup>10–13</sup>

Here, we use a first principles-based effective Hamiltonian<sup>14–16</sup> to study the effect of substrate-induced clamping and compressive epitaxial strain on the EC temperature change in BaTiO<sub>3</sub>. In the effective Hamiltonian,

the structural degrees of freedom are described via a small number of collective modes: a polar *soft mode* related to the ferroelectric distortion in each unit cell, and several local and global strain variables. All parameters of the corresponding energy expression can be calculated from first principles electronic structure calculations. This allows to perform temperature-dependent simulations for relatively large system sizes without having to resort to empirical fitting of experimental data. The effective Hamiltonian approach has previously been used to study the EC effect in several bulk materials,<sup>17–20</sup> and good agreement with experimental observations has been found.

We perform molecular dynamics (MD) simulations for the effective Hamiltonian using the FeRAM code developed by Nishimatsu, *et al.*<sup>16</sup> To simulate BTO, we use the set of parameters obtained in Ref. 21 using the generalized gradient approximation (GGA) according to Wu and Cohen.<sup>22</sup> It has been shown that this exchange-correlation energy functional leads to more accurate structural parameters for BTO than previous calculations based on the local density approximation (LDA).<sup>21</sup> We note, however, that in contrast to Ref. 16 we do not apply any empirical pressure corrections in our calculations.

In order to simulate clamping to a (001)-oriented substrate, we fix certain components of the homogeneous strain tensor in the effective Hamiltonian ( $\eta_1 = \eta_2 = \eta = \text{const.}$  and  $\eta_6 = 0$  in standard Voigt notation), while all other components as well as all inhomogeneous strain variables are optimized with respect to the current soft mode configuration in each MD step. We use a simulation box of  $16 \times 16 \times 16$  perovskite unit cells and periodic boundary conditions in all three cartesian directions, i.e. our simulations correspond to “strained bulk”. This allows us to focus on the pure strain effect while excluding any finite size, surface, or interface effects. We use 60,000 MD steps to thermalize the system and then a further 40,000 steps to average over the required properties with a time step of 2 fs per MD iteration.

To provide an appropriate reference for our calculations of the EC effect in strained BTO, we first

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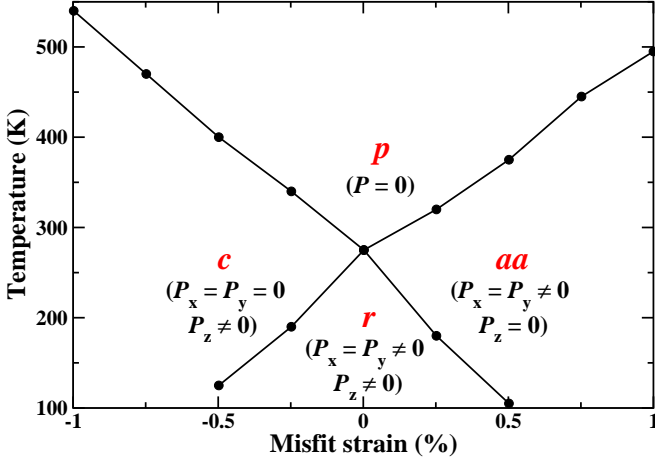


FIG. 1. Temperature-strain phase diagram for epitaxially strained BTO: transition temperatures are plotted as a function of misfit strain. Here,  $p$  denotes the high-temperature paraelectric phase, while  $c$ ,  $r$ , and  $aa$  denote the three ferroelectric phases with different polarization directions.

establish the strain-temperature phase diagram for the Wu/Cohen-GGA parameterization of the effective Hamiltonian. We calculate all components of the total polarization as function of temperature for each value of strain, and from this we identify the transition temperatures corresponding to the various phase transitions. Similar to Ref. 9, we use the lattice constant immediately above the cubic to tetragonal phase transition in the unstrained bulk calculation ( $a_0 = 3.995 \text{ \AA}$ ) as reference to define zero misfit strain. The resulting phase diagram is shown in Fig. 1.

The calculated phase diagram compares very well with the one obtained in Ref. 9 using an LDA parameterization of the effective Hamiltonian. Note that in contrast to Ref. 9 we do not apply any empirical pressure corrections in the effective Hamiltonian. At high temperatures, strained BTO is paraelectric ( $p$ ), while at lower temperatures three different ferroelectric phases with different orientations of the polarization vector  $P$  occur ( $c$ ,  $r$  and  $aa$ , see Fig. 1). All phase boundaries meet in one point at  $T \approx 270 \text{ K}$  and zero strain, in good agreement with previous studies.<sup>8,9</sup>

Next, we compute the EC temperature change  $\Delta T$  at different working temperatures for bulk BTO and mechanically clamped BTO under different compressive strains (including zero strain). We use an indirect approach to calculate the EC temperature change (see e.g. Refs. 19 and 20). This approach is based on the following Maxwell relation:

$$\left. \frac{\partial S}{\partial E} \right|_T = \left. \frac{\partial P}{\partial T} \right|_E, \quad (1)$$

which relates the isothermal entropy change due to an applied electric field to the temperature dependence of the electric polarization at constant electric field. The latter can be calculated using the effective Hamiltonian

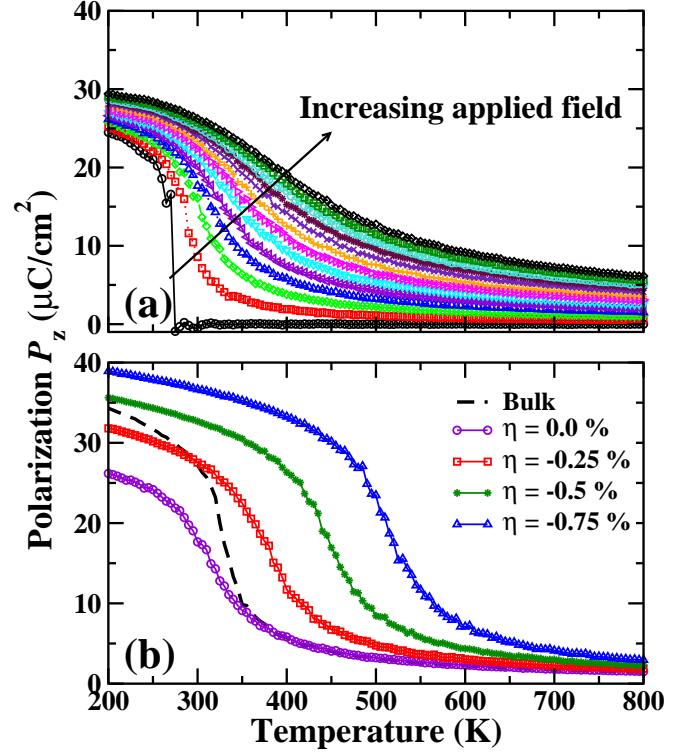


FIG. 2. (a) Polarization as function of temperature for strained BaTiO<sub>3</sub> under 0.0% misfit strain at various applied fields starting from 0 to 300 kV/cm in steps of 25 kV/cm. (b) Polarization as function of temperature at an applied field of 75 kV/cm for unstrained bulk and clamped systems at different strains. Only the polarization component along the applied field direction,  $P_z$ , is plotted.

approach. Here,  $S$  and  $T$  denote the entropy and temperature of the system,  $P$  is the total polarization, and  $E$  is the applied electric field. The EC temperature change  $\Delta T$  is then given by:

$$\Delta T = - \int_{E_1}^{E_2} \frac{T}{C_{p,E}} \left( \frac{\partial P}{\partial T} \right)_E dE, \quad (2)$$

where  $C_{p,E}$  is the specific heat at constant pressure and constant electric field. We have used a temperature-independent value of  $C_p = 2.53 \text{ Jcm}^{-3}\text{K}^{-1}$  for the specific heat, which corresponds to the experimental value measured at room temperature.<sup>23</sup>  $E_1$  and  $E_2$  are the initial and final electric fields. We focus on the temperature range of the paraelectric to ferroelectric transition, i.e.  $p$  to  $r$  ( $c$ ) for zero (nonzero) strain in Fig. 1, where the strongest EC effect can be expected.<sup>2,19,24</sup>

Fig. 2(a) shows the calculated temperature dependence of the electric polarization for zero applied strain, i.e. pure clamping, and different electric fields up to a maximum of 300 kV/cm. Fields of this magnitude are typically applied in thin film samples.<sup>3,25</sup> The external field is applied along the [001] direction, i.e. perpendicular to the direction of clamping. There is a sharp phase

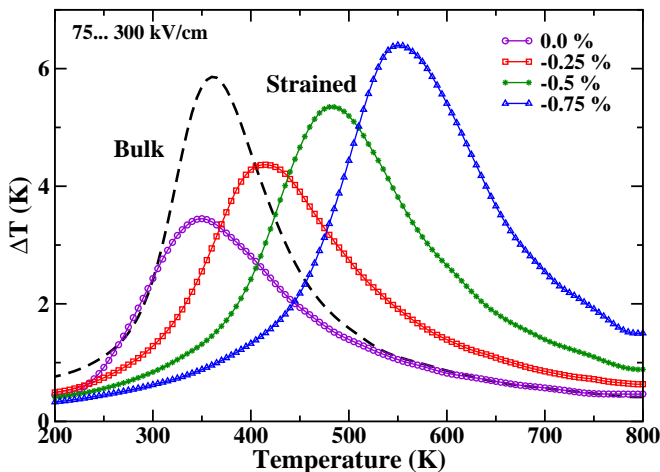


FIG. 3. The electrocaloric temperature change as a function of temperature: shown here for free (dashed line) and strained bulk BaTiO<sub>3</sub> with misfit strain equal to 0.0 % (circles), -0.25 % (squares), -0.5 % (stars) and -0.75 % (triangles).  $\Delta T$  is calculated for a variation of the applied field from 75 kV/cm to 300 kV/cm.

transition from paraelectric to ferroelectric (*r*-phase) in absence of the external field. In presence of the field, the transition temperature first shifts to slightly higher temperatures and then the phase transition disappears and the system shows a smooth dependence of polarization on temperature (compare also to Refs. 24 and 26). Qualitatively similar behavior is observed for the free bulk case and for other strain values, only the corresponding zero-field transition temperature is shifted according to Fig. 1 and the magnitude of the low temperature polarization increases for increasing strain as shown in Fig. 2(b).

Note that the results in Fig. 2 are obtained from statistical averaging over many MD steps and therefore contain small statistical fluctuations. To compute  $\partial P/\partial T$ , we therefore fit the polarization versus temperature using smoothing cubic spline functions. Due to the rather sharp transition for small electric fields (first order in the free bulk case) the derivative is ill-defined around the transition temperature, and we therefore use  $E_1 = 75$  kV/cm and  $E_2 = 300$  kV/cm for the calculation of the EC temperature change  $\Delta T$  in Eq. (2), i.e. we exclude small electric fields.

The resulting  $\Delta T$  is shown in Fig. 3 for the various cases. For bulk BTO, a maximum  $\Delta T$  of about 5.9 K is reached at  $T \approx 360$  K, i.e. 65 K above the calculated zero field transition temperature. This agrees well with previous calculations.<sup>20</sup> Clamping by the substrate (at zero strain) strongly reduces the EC temperature change to about 3.4 K, consistent with previous results based on phenomenological theory.<sup>26</sup> Note that for clamped BTO at zero strain, the ferroelectric phase (*r*) has a non-zero polarization in all three crystallographic directions. However, only the component along the applied field direction ( $P_z$ ) contributes to the EC temperature change.

Increasing compressive misfit strain leads to a strong increase of the peak value of  $\Delta T$  compared to the clamped zero strain case. Simultaneously, the temperature at which the maximum  $\Delta T$  is observed also increases. This shift of the peak position of  $\Delta T$  is due to the increase of the paraelectric-to-ferroelectric transition temperature with compressive strain (see Fig. 1), since the largest  $\Delta T$  is always observed just above the ferroelectric transition temperature, i.e. where the slope  $\partial P/\partial T|_E$  is steepest. The increase of the maximum  $\Delta T$  with compressive strain can also be related to the increase of the ferroelectric transition temperature, since it is to a large extent due to the factor  $T$  in Eq. (2). Physically, this means that, according to the relation  $\Delta Q = T\Delta S$ , the amount of heat  $\Delta Q$  connected with a certain entropy change  $\Delta S$  is larger at higher temperatures, and therefore the EC temperature change is larger at higher temperatures (for the same  $\Delta S$ ). In addition, there is a small increase in  $\partial P/\partial T|_E$  with compressive strain, which is related to the increase of the spontaneous polarization with compressive strain (see Fig. 2(b)), and which (to a smaller extent) also contributes to the increase of  $\Delta T$ .

Interestingly, at strain values as small as -0.75 %, the maximum  $\Delta T$  becomes larger than in the bulk case, and reaches a value of 6.4 K. Previous experimental studies have reported that BTO films with thicknesses up to 200 nm can be grown coherently for epitaxial strains as large as -1 %, <sup>7</sup> which implies that a large EC effect can be expected in epitaxially grown films of BTO. We also note that, due to the strong shift of the transition temperature, strain can also provide an effective tool to optimize the EC effect at a given operating temperature. For example, for a device that has to operate around 400 K, strained BTO with  $\eta = -0.25$  % would be the best choice, even though a larger peak value of  $\Delta T$  can be achieved for  $\eta = -0.75$  %.

One should note that while a large and tunable EC effect can be achieved in thin films, a major obstacle for using thin films in cooling devices is that the available volume of the EC material is very small and therefore only small amounts of heat can be transferred. One possibility to circumvent this problem could be the use of multilayer geometries such as e.g. the one discussed in Ref. 25.

In summary, we have used MD simulations for a first principles-based effective Hamiltonian to study the EC effect in epitaxially strained bulk BTO. We have shown that clamping by the substrate (at zero strain) strongly reduces the EC effect compared to bulk BTO, whereas moderate compressive strain leads to a strong enhancement of the EC effect as well as a strong shift of the temperature at which the maximal EC temperature change is observed. Thus, misfit strain can be utilized in two ways – (i) to enhance the EC temperature change and (ii) to achieve a maximal effect in a temperature range of interest for a given application.

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